RADICAL REACTIONS OF ETHYL ORTHOFORMATE WITH 1-HEXENE

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No reactions of orthoesters with unsaturated compounds have been reported. Homolytic reactions of ethyl orthoformate in the presence of tert-butyl peroxide at 130-150°C have been described. It was shown that the radicals formed undergo fragmentation to give diethyl carbonate, ethyl formate, and acetaldehyde [1]:

 $\begin{array}{c} \mathrm{HC}(\mathrm{OCH}_{2}\mathrm{CH}_{3})_{3} \xrightarrow{\mathrm{RO}^{*}k_{\mathrm{CH}}} \dot{\mathrm{C}}(\mathrm{OCH}_{2}\mathrm{CH}_{3})_{3} \\ \hline k_{\mathrm{CH}_{2}} & \dot{\mathrm{C}}(\mathrm{OCH}_{2}\mathrm{CH}_{3})_{2}\mathrm{O}\dot{\mathrm{C}}\mathrm{HCH}_{3} \\ \hline \dot{k}_{\mathrm{CH}_{2}} & \mathrm{HC}(\mathrm{OCH}_{2}\mathrm{CH}_{3})_{2}\mathrm{O}\dot{\mathrm{C}}\mathrm{HCH}_{3} \\ \hline \dot{k}_{\mathrm{CH}_{2}} & \mathrm{HC}(\mathrm{OCH}_{2}\mathrm{CH}_{3})_{2}\mathrm{O}\dot{\mathrm{C}}\mathrm{HCH}_{3} \\ \hline \dot{\mathrm{C}}(\mathrm{OCH}_{2}\mathrm{CH}_{3})_{2}\mathrm{O}\dot{\mathrm{C}}\mathrm{HCH}_{3} & \xrightarrow{-\mathrm{CH}_{2}\mathrm{CH}_{2}} \mathrm{H}\dot{\mathrm{C}}(\mathrm{O}\mathrm{CH}_{2}\mathrm{CH}_{3})_{2} \\ \mathrm{H}\dot{\mathrm{C}}(\mathrm{O}\mathrm{CH}_{2}\mathrm{CH}_{3})_{2}\mathrm{O}\dot{\mathrm{C}}\mathrm{HCH}_{3} & \xrightarrow{-\mathrm{C}_{2}\mathrm{H}_{5}} \mathrm{H}\dot{\mathrm{C}}(\mathrm{O}\mathrm{O}\mathrm{C}_{2}\mathrm{H}_{5} \\ \hline \mathrm{H}\dot{\mathrm{C}}(\mathrm{O}\mathrm{CH}_{2}\mathrm{CH}_{3})_{2} & \xrightarrow{-\mathrm{C}_{3}\mathrm{H}_{5}} \mathrm{H}\mathrm{C}(\mathrm{O}\mathrm{O}\mathrm{C}_{2}\mathrm{H}_{5} \end{array}$ 

A study of the relative kinetics of this reaction showed that the reactivity of the orthoester at the H-C(OR); bond was greater by an order of magnitude than the C-H bond in CH<sub>2</sub>O [2].

We here report a study of the radical addition of ethyl formate to 1-hexene in the presence of tert-butyl peroxide (140°C), in which a variety of interesting features and behavior of the intermediate radical-adducts was observed. Results were obtained which enabled the relative rates of addition to 1-hexene and fragmentation of the radicals  $C(OC_2H_5)_3$  and HC. (OC2H5)2OCHCH3 to be compared. The homolytic reaction of ethyl orthoformate with 1-hexene gave as the main product not the orthoester (II), but the carbonate  $CH_3CH_2OC(0)OCH(CH_3)C_6H_{13}$ (I) (route 2). In addition to (I), there were formed fragmentation products of the intermediate radicals together with small amounts of a ketone which is assigned the structure  $C_{6}H_{13}C(0)C_{7}H_{15}$  (III). The fragmentation products (diethyl carbonate and ethyl formate) were identified by GLC by comparison with authentic samples. The structures of the preparatively isolated adduct (I) and ketone (II) were confirmed by their <sup>13</sup>C NMR spectra (Table 1). The

				δ <b>,p</b> pm f	rom TMS
Compound	C(O)	CH2O	сно	CH3	CH <sub>2</sub>
$HC(OCH_2CH_3)_3^*$	111,6	58,3	_	13,9	
$HC(O)OCH_2CH_3 *$	161,0	59,4	-	13,6	-
$C(O) (OCH_2CH_3)_2 *$	154,7	62,8		13,9	_
$7 \underbrace{12^{2} - 45}_{CH_3CH_2OC(0)OCHCH_2(CH_2)_3CH_2CH_3} + \underbrace{12^{2} - 45}_{CH_3} + \underbrace{12^{2} - 45}_{CH$	154,0	62,4	73,7	13,8(7) 14,1(6) 19,6(8)	$\begin{array}{c} 35,7(1), \ \ 31,6(2),\\ 28,9(3)\\ 25,1(4),\ 22,4(5) \end{array}$
$CH_{3}CH_{2})_{4}CH_{2}C(0)CH_{2}(CH_{2})_{5}CH_{3}$ (III)	204,0	_	-	13,8	$\begin{array}{c} 48,1(1),\ 33,3,33,6,\\ 29,6,\ 29,4,\ 31,7,\\ 28,7,\ 26,4,\ 22,7,\\ 22,4(2{\rightarrow}6) \end{array}$
*Reference compounds. †n <sup>20</sup> <sub>D</sub> 1.4197, d <sup>20</sup> <sub>4</sub> 0.8859, N	(R <sub>four</sub>	nd =	58.4,	MRcale	= 57.5.

<sup>13</sup>C NMR Spectra of Reference Compounds and Compounds TABLE 1. Obtained

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Initiator, tert-Butyl Peroxide (140°C, 

 TABLE 2. Addition of Orthoformate Ester (S) to 1-Hexene (M).

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Amounts,	mmoles	Conve.	rsion, 껴		[M]e	Distribu	tion of reaction	n products, mo	ole %	$k_{\mathrm{CH}}^*$	kf .
W	s	М	ß	(S)av	۸ <i>و</i> (۲۰۰۰ ۱	$HG(O)OC_2H_5$	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CO	adduct (I)	ketone (III)	k CH2	ha mole/liter
0,5	10	25,2	14,4	0,05	0,12	35,9	57,7	5,8	0,6	1,4	0,76
0,6	10	22	14,2	0,06	0,14	31	62,0	7,0	1	1,7	0,63
<b>€</b> ni	10	20,8	15,5	0,1	0,24	31,9	57,9	9,6	0,6	1,4	0,83
5	10	19,4	15,4	0,2	0,47	23,3	59,5	15,5	1,7	1,5	0,71
ŝ	10	7,1	5,6	0,3	0,77	20,5	53,8	20,6	5,1	1,3	0,77
4	10	12,8	10,5	0,4	1,04	15,5	52,1	26,8	5,6	1,5	0,60
2	10	8,2	10,3	0,5	1,19	18,7	54,7	20,3	6,3	1,4	1,1
									Mean	$1,5{\pm}0,1$	$0,77 \pm 0,1$
* <sup>k</sup> CH	[(C2HSC [HC(0)0C2	) <sub>1</sub> co] H <sub>6</sub> ] + [I]	$\frac{k_{\rm f}}{k_{\rm a}} = \frac{[M]}{a}$	[HC(0)OC <sub>2</sub> H <sub>5</sub> ]							

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formation of adduct (I) is accounted for by a route involving rearrangement of the radicaladduct A, with 1,5-migration of hydrogen and fragmentation of the isomerized radical-adduct with elimination of the ethyl radical

$$\begin{array}{c|c} HC(OC_{2}H_{5})_{2}O\dot{C}HCH_{3} + C_{4}H_{9}CH = CH_{2} \xrightarrow{k_{a}} HC(OC_{2}H_{5})_{2}OCH(CH_{3})CH_{2}\dot{C}HC_{4}H_{9}(\dot{A}) \\ & & \downarrow \\ & & \downarrow \\ & & \downarrow \\ \hline & & \downarrow \\ \hline & & \downarrow \\ \hline & & \downarrow \\ \dot{C}(OC_{2}H_{5})_{2}OCH(CH_{3})C_{6}H_{13} & (II) \\ & & \downarrow \\ \hline & & \downarrow \\ \dot{C}(OC_{2}H_{5})_{2}OCH(CH_{3})C_{6}H_{13} & (II) \\ \hline & & \downarrow \\ \hline & & \downarrow \\ \hline & & \downarrow \\ \dot{C}(OC_{2}H_{5})_{2}OCH(CH_{3})C_{6}H_{13} & (II) \\ \hline & & \downarrow \\ \hline & & \downarrow \\ \hline & & \downarrow \\ \dot{C}(OC_{2}H_{5})_{2}OCH(CH_{3})C_{6}H_{13} & (II) \\ \hline & & \downarrow \\ \hline \\ \hline & & \downarrow \\ \hline \hline \\ \hline & & \downarrow \\ \hline \hline \\ \hline \hline \\ \hline & \hline$$

No orthoester of heptanoic acid was found in the reaction mixture, indicating that the fragmentation of the  $\dot{C}(OC_2H_5)_3$  radical was much more rapid than its addition to 1-hexene. We have previously observed similar behavior in a study of the radical telomerization of ethylene with straight-chain acetals [3], in which it was found that the  $\dot{C}H(OCH_3)_2$  radical did not react with ethylene to give the acetals of higher aldehydes, but fragmented completely to give methyl formate. The rapid rearrangement of the radical-adduct A with 1,5-hydrogen transfer, as shown by the absence of the orthoester (II) from the reaction products, perhaps results from the ease of homolysis of the H-C( $OC_2H_5$ )<sub>3</sub> bond and also from the nature of the six-membered transition state which incorporates an oxygen atom. The formation of the ketone (III) with two unbranched hydrocarbon chains of differing lengths (<sup>13</sup>C NMR data) suggests that the reaction proceeds in part at a C-H bond of the methyl group

The proportion of the ketone (III) was no more than 1-6% of the total reaction products (Table 2), i.e., this reaction pathway is not of great importance. Experiments carried out under strictly controlled conditions over the range of ratios of 1-hexene to orthoester 0.05-0.5 enabled the ratio of the rate constants for the removal of hydrogen from C-H groups  $(k_{CH})$  and  $CH_2O$   $(k_{CH_2})$  to be compared. This ratio describes the relative reactivities of these groups (Table 2). The value found for this ratio (1.5) is close to the ratio of these constants found in a study of the fragmentation of the orthoester in the presence of tertbutyl peroxide [2]. In the orthoformate ester molecule, there are six C-H bonds in CH20 groups per formyl C-H bond. Bearing in mind this statistical factor, the formyl C-H bond is an order of magnitude more reactive than the C-H bond in the alkoxy group. In these experiments, we also determined the rate constant for the fragmentation (kf) and addition (ka) of the  $HC(OC_2H_5)_2OCHCH_3$  radical to 1-hexene. It was found to be close to unity (0.8 mole/ liter). The amounts of diethyl carbonate formed in the experiments were sensibly constant, and were not dependent on the hexene-orthoester ratio or the yield of adduct (I) (Table 2), showing that the yield of diethyl carbonate is determined by the ratio  $k_{CH}/k_{CH_2}$ . However, as the proportion of the adduct (I) increased, the proportion of ethyl formate decreased, although the sum of their yields remained approximately constant. These findings provide support for the formation of adduct (I) by the route described above: During its formation, as a result of secondary reactions of the diethyl carbonate present in the reaction mixture with 1-hexene, any increase in the yield of the adduct should result in a substantial reduction in the proportion of ethyl carbonate:

$$C(O) (OC_{2}H_{5})_{2} \xrightarrow{RO} C(O) (OC_{2}H_{5}) OCHCH_{3}$$

$$C(O) (OC_{2}H_{5}) OCHCH_{3} + CH_{2} = CHC_{4}H_{p} \xrightarrow{DH} C(O) (OC_{2}H_{5})OCH(CH_{3})C_{6}H_{13}$$
(I)

The structure of adduct (I) was confirmed by the presence in its <sup>13</sup>C NMR spectrum (Table 1) of signals typical of the functional group <sup>13</sup>C(0)(OR)<sub>2</sub>, and the <sup>13</sup>CHO and <sup>13</sup>CH<sub>3</sub>CH groups, confirming the addition of 1-hexene at the orthoester CH<sub>2</sub>O, and the presence of a signal for the CH<sub>3</sub><sup>13</sup>CH<sub>2</sub>O group shows that the carbonate molecule retains one of the two ethoxy groups. The chemical shifts of the remaining signals, and the ratios of their intensities, are in accordance with the assignments made. The ketone (III) showed signals characteristic of the <sup>13</sup>CO and <sup>13</sup>CH<sub>2</sub>C(O)<sup>13</sup>CH<sub>2</sub> groups, the latter being twice as intense.

## EXPERIMENTAL

<sup>13</sup>C NMR spectra were obtained on a Bruker-Physik HX-90 spectrometer, operating frequency 22.635 Hz, internal standard CCl<sub>4</sub>, chemical shifts measured relative to TMS.

Preparative GLC was carried out on a PAKhV-01 apparatus, column 1200  $\times$  9 mm with 15% SKTFT-50 on Chromatone N-AW, and GLC analyses were carried out on an LKhM-8MD-5, column 3000  $\times$  3 mm with 5% SKTFT on Chromatone N-AW, catharometer, helium.

Addition of Ethyl Orthoformate to 1-Hexene. Preparative experiments were carried out in sealed glass ampuls (30 ml) under nitrogen, with 18 g of the orthoester, 10 g of 1-hexene, and 2 g of tert-butyl peroxide. The reaction mixture was heated in an oil bath at 140°C for 2 h, the ampuls being rotated in metallic sleeves. Eight similar experiments were carried out, and the products combined. Following removal of the starting materials by distillation, there was obtained 18.1 g of mixed products. This mixture was fractionated to obtain narrow fractions of adduct (I) and ketone (III) (weights of fractions, 4.9 g), and the narrow fractions were further purified by preparative GLC.

The kinetic experiments were carried out similarly, in 3-ml ampuls. The experimental conditions and GLC analyses are shown in Table 2.

## CONCLUSIONS

1. The homolytic addition of ethyl orthoformate to 1-hexene is accompanied by fragmentation and isomerization of the intermediate radicals, as a result of which the adduct ethyl 2-octyl carbonate is formed.

2. The formyl C-H bond in ethyl orthoformate is approximately an order of magnitude more reactive than the  $\alpha$ -C-H bond of the ethoxy group.

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